

# ISOTHERMAL $n$ th ORDER REACTION IN CATALYTIC PELLETS EFFECT OF EXTERNAL MASS TRANSFER RESISTANCE

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**Abstract**—The effectiveness factor for the isothermal power-law decomposition of a reactant within symmetrical catalytic pellets is obtained from the solution of a single first order differential equation. The effects of external mass transfer are taken into account, as well as the effect of simple types of non-uniform distribution of the catalyst within the particle.

For fractional and negative reaction orders there are solutions with zero concentration in a central region of the particle. For negative reaction orders intervals of multiplicity of solutions are found.

## 1. INTRODUCTION AND FORMULATION

We present in this paper an analysis of the isothermal response of a symmetrical catalyst particle where a  $n$ th order decomposition reaction is taking place, including in the analysis the effect of the external resistance to mass transfer. The problem has received considerable attention in the literature, see the review by Aris[1], where the problem is stated as to find the solution of the equation

$$u_{xx} + jx^{-1}u_x = \phi^2 u^n \quad (1)$$

with the boundary conditions

$$u_x(0) = 0, \quad u_x(1) = \nu(1 - u_s) \quad (2)$$

where  $u$  and  $x$  are the concentration and distance to the particle center, made non-dimensional with respect to the interstitial concentration and particle radius. The subscript  $s$  refers to conditions at the particle surface;  $\phi$  is the Thiele modulus,  $\nu$  the Sherwood number, and  $j = 0, 1$  and  $2$  for slabs, cylinders and spheres.

The most important output from the solution is the non-dimensional observed reaction rate per particle  $\psi$  and the effectiveness factor  $\eta$ , defined by

$$\psi = \eta\phi^2 = (j+1)u_x(1). \quad (3)$$

An analysis of the relation between  $\eta$ ,  $\phi$ ,  $n$  and  $\nu$  for the planar case was given by Metha and Aris[2], including a discussion of the conditions for existence and multiplicity of the solution. We shall consider other symmetrical geometries, and we shall make, as they did, a natural extension of the problem by writing the reaction term of eqn (1) equal to zero for  $u = 0$ , looking for solutions not only of type (a), with continuous derivatives of all orders with a non zero concentration  $u_0$  at the particle center, but also for solutions of type (b), existing

in the range  $-1 < n < 1$ , continuous and with continuous first derivatives, so that there are no jumps in concentration or in mass flux, showing a core of radius  $x_0$  at the particle center where  $u = 0$ .

We shall begin by analyzing in Section 2 the limiting case  $\nu \rightarrow \infty$ , when the external mass transfer resistance is negligible, and the boundary condition of eqn (2) reduces to the Dirichlet form  $u_s = 1$ . We shall show how in this case the relation between  $\psi$  and  $\phi^2$  is given directly by the solution of an ordinary differential equation, where  $n$  and  $j$  appear as parameters; the qualitative theory of differential equations can then be used, as Joseph and Lundgren[3] did in a similar problem, to describe the main characteristics of the relation  $\psi = \psi(\phi^2, n, j)$ , including the conditions for existence and multiplicity of the solutions. We shall see in Section 3 how the results can be used to account for the effect of external mass transfer resistance.

## 2. SOLUTION WITHOUT EXTERNAL MASS TRANSFER RESISTANCE

Equation (1) is invariant under the continuous group of transformations

$$u \rightarrow \alpha u, \quad x \rightarrow \alpha^{(1-n)/2} x \quad (4)$$

that was also used by Volkman and Kehat[4] to simplify the numerical calculation of the relation  $\psi = \psi(\phi)$  for the Dirichlet problem. We shall use this fact to write eqn (1) as an autonomous system of equations using as dependent variables

$$\omega = (x/u)u_x \text{ and } \theta = \phi^2 x^2 u^{n-1}, \quad (5)$$

also invariant under the same group, and taking at  $x = 1$ , the values  $\psi(j+1)$  and  $\phi^2$ , respectively, in the limiting case  $\nu \rightarrow \infty$  when  $u_s = 1$ . As independent variable we

choose

$$z = \ln(u/u_0) \text{ or } t = \ln(x/x_0) \quad (6)$$

for problems (a) and (b), respectively. Then eqn (1) is replaced by the autonomous system

$$\begin{aligned} \frac{d\omega}{dz} &= \frac{d\omega}{\omega dt} = \frac{\theta}{\omega} - \omega + 1 - j \\ \frac{d\theta}{dz} &= \frac{d\theta}{\omega dt} = \frac{2\theta}{\omega} + (n-1)\theta \end{aligned} \quad (7)$$

to be solved for problem (a) with the initial conditions

$$\omega/2z = \theta/2(j+1)z = 1 \text{ for } z \rightarrow 0, \quad (8a)$$

when leaving the critical point  $\omega = \theta = 0$ , resulting from the conditions at the particle center. The critical point is a saddle if  $j = 1$  or  $2$ , and it is a node, that is left following the exceptional direction, if  $j = 0$ . When eqns (7) are integrated, for given  $n$  and  $j$ , with these initial conditions† the resulting single-valued functions  $\omega(z)$  and  $\theta(z)$  provide, if the Dirichlet condition  $u(1) = 1$  is taken into account, a parametric representation, with parameter  $u_0$ , of the relation between  $\psi$  and  $\phi^2$ ; namely,

$$\psi/(j+1) = \omega, \quad \phi^2 = \theta \text{ at } z = -\ln u_0. \quad (9a)$$

For problem (b), eqns (7) must be solved with the asymptotic condition

$$(1-n)t\omega/2 = (1-n)^2 t^2 \theta/2(1+n) = 1 \text{ for } t \rightarrow 0 \quad (8b)$$

obtained from the continuity conditions at  $x = x_0$ . The single-valued solutions  $\omega(t)$ ,  $\theta(t)$  for given  $n$  and  $j$  provide a parametric representation, with the parameter  $x_0$ , of the relations between  $\phi^2$  and  $\psi$ , when we take again into account the condition  $u(1) = 1$ ; namely,

$$\psi/(j+1) = \omega, \quad \phi^2 = \theta \text{ at } t = -\ln x_0. \quad (9b)$$

No solutions of type (b) exist outside the interval  $-1 < n < 1$ , as it has also been found by Metha and Aris[2]; the reaction rate grows too fast to infinity, if  $n \leq -1$ , or decreases too fast to zero, if  $n \geq 1$ , when  $u \rightarrow 0$ , to allow for the existence of solutions with  $u$  and  $u_x$  approaching zero simultaneously at a finite radius  $x_0$ .

The concentration distribution within the particle can also be obtained easily from the solution if  $e^z$  is represented in terms of  $\sqrt{(\theta \exp(1-n)z)}$  for problem (a) and  $e^t$  in terms of  $\{\theta \exp(-2t)\}^{1/(n-1)}$  for problem (b).

The phase plane path  $\omega(\theta)$  corresponding to the solutions of type (a) or (b) can be calculated by integrating the differential equation

$$\frac{d\omega}{d\theta} = \frac{\theta - \omega^2 + (1-j)\omega}{2\theta + (n-1)\omega\theta} \quad (10)$$

with the initial condition  $\theta/\omega = j+1$ , when  $\theta \rightarrow 0$ , for problem (a), or the asymptotic condition  $\theta/\omega^2 = (n+1)/2$ , when  $\theta \rightarrow \infty$ , for problem (b). If  $\theta = \theta(\omega, n, j)$  is the solution, the relation between  $\phi^2$  and  $\psi$  when the external mass transfer resistance is neglected is given by

$$\phi^2 = \theta\{\psi/(j+1), n, j\}. \quad (11)$$

The form of this relation is determined by the character of the critical points of eqns (7) or (10). In particular, for values of  $-1 < n < 1$ , the solution approaches, when  $z \rightarrow \infty$  or  $t \rightarrow \infty$ , the critical point  $(\theta_c, \mu_c)$ , given by

$$\omega_c = 2/(1-n), \quad \theta_c = 2\{j-1+2/(1-n)\}/(1-n), \quad (12)$$

which is a node (approached along the regular direction), unless  $n < 0$  for  $j = 1$ , or  $n < (11-8\sqrt{2})/7$  for  $j = 2$ , when it is a stable focus; thus the curve  $\theta(\omega)$  for these last values of  $n$  spirals around the critical point and a large number of solutions exist for  $\phi^2$  to close to  $\theta_c$ . These solutions approach the critical solution of eqn (1) for  $\phi^2 = \theta_c$ , obtained from eqn (5) with  $\theta = \theta_c$ . For  $n < -1$  and  $j = 0$ ,  $\omega_c$  becomes negative and the solutions of type (a) approach, when  $z \rightarrow \infty$ , a second critical point, a stable node, located at  $\theta = 0$ ,  $\omega = 1$ .

The limiting form of the solution of type (b) for  $(n+1) \rightarrow 0^+$  has two branches if  $j = 1$  or  $2$ ; one is the solution of type (a) for  $n = -1$ , the other is the line  $\theta = 0$ ,  $\omega > 0$ .

Figure 1 shows the relation  $\omega(\theta)$  for spherical particles and some representative values of  $n$ , with solid lines and dashed lines for solutions of type (a) and (b) respectively. These curves give also  $\psi/3$  in terms of  $\phi^2$  in the case  $\nu \rightarrow \infty$ . Points corresponding to several values of  $u_0$  and  $x_0$  have also been shown in the Figure.

The effectiveness factor  $\eta$  is given by  $\omega/\theta$  in the limit  $\nu \rightarrow \infty$ ; Fig. 2 shows  $\eta$  as a function of  $\phi^2/(j+1)^2$  with thick lines for slabs and with thin lines for spheres.

There is no difficulty in extending the analysis to cases where the catalytic activity is non-uniform, if it can be represented by introducing a factor  $x^k$  in the reaction term of eqn (1), invariant again under a new transformation group; the same factor should then be introduced in the definition of  $\theta$ , and the term  $2\theta$  replaced by  $(2+k)\theta$  in eqn (10), that should be solved for problem (a) with the initial condition  $(k+j+1)\mu/\theta = 1$  for  $\theta \rightarrow 0$ .

### 3. EFFECT OF EXTERNAL MASS TRANSFER RESISTANCE

For finite values of  $\nu$ , when  $u_s \neq 1$ , the relations (9) must be replaced by  $\omega = \psi/(j+1)u_s$ ,  $\theta = \phi^2 u_s^{n-1}$ , or, when the surface condition of eqn (2) is taken into account, by

$$\psi/(j+1) = \nu\omega/(\omega + \nu), \quad \phi^2 = (1 + \omega/\nu)^{n-1}\theta \quad (13)$$

and

$$u_s = \nu/(\omega + \nu), \quad \eta = (j+1)\nu^n/\theta(\nu + \omega)^n \quad (14)$$

which provide a parametric representation, with  $\omega$  as

†For  $n = 0$ :  $\omega = \theta/(j+1) = 2(1-e^{-z})$ ; for  $n = 1$ ,  $j = 2$ :  $\omega = \sqrt{(\theta)/\tanh \sqrt{(\theta)-1}}$ ,  $z = \ln(\sinh \sqrt{(\theta)/(\theta)})$ .

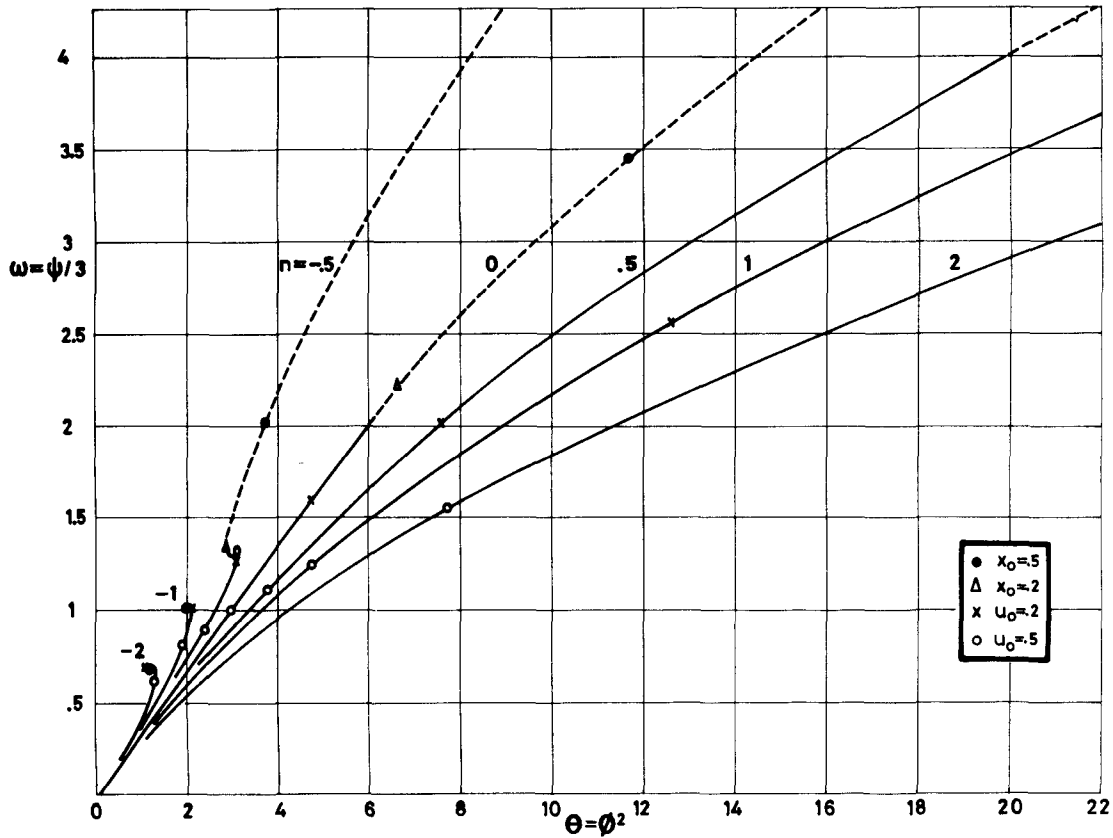


Fig. 1. The relation  $\omega(\theta)$  for  $j=2$ , or  $\psi/3$  as a function of  $\phi^2$  for spherical pellets without external mass transfer resistance; for problem (a) with solid lines, and for problem (b) with dashed lines.

parameter, for the relations giving  $\psi$ ,  $u_s$  and  $\eta$  in terms of  $\phi$ ,  $\nu$ ,  $n$  and  $j$ .

The function  $\psi(\phi)$  can be multivalued if  $n < 0$ , for values of  $\phi$  within a multiplicity interval  $(\phi_m, \phi_M)$  which depends on  $\nu$ . The extremum values of  $\phi$  are given by the condition  $d\phi/d\psi = 0$ ; according to eqns (10), (12) and (13) we obtain

$$\nu = \frac{\theta - \omega\theta_c/\omega_c}{\omega_c - \omega}. \quad (15)$$

Thus the points of intersection of the curve  $\omega(\theta)$  in the plane  $(\theta, \omega)$  with the straight line joining the critical point  $(\theta_c, \omega_c)$  and the point  $(\nu\omega_c, 0)$  give the values of  $\theta$  for which changes in the multiplicity of the solution of the Robin problem occur. The relation  $\psi(\phi)$  is thus found to be single-valued for  $n > 0$ , because the curvature of  $\omega(\theta)$  is negative, and also if  $\nu > \{1 - n - \sqrt{(1 + 22n - 7n^2)}/2(1 - n)\}$ ,  $j=2$  and  $(11 - 8\sqrt{2})/7 < n < 0$ . In any other case there are multiple solutions in an interval that grows in size with increasing values of  $\nu$ .

In the important practical case when  $\nu \gg 1$ , there are two reaction regimes, according to the first of the eqns (13). In a first regime  $\omega$  is of order unity,  $1 - u_s \sim 1/\nu$  is small, while  $\psi$  and  $\phi^2$  are given by  $(j+1)\omega$  and  $\theta$ , corresponding to negligible effects of the external mass transfer resistance as analysed in Section 2. In a second

regime  $\omega$  is large so that  $\omega/\nu = \xi$  is of order unity and eqns (13) simplify to

$$\frac{\psi}{(j+1)\nu} = \frac{\xi}{1+\xi}, \quad \left(\frac{\phi}{\nu}\right)^2 = \frac{n+1}{2} \xi^2(1+\xi)^{n-1} \quad (16)$$

a parametric representation of the relation between  $\phi/\nu$  and  $\psi/\nu$ , which can also be written explicitly; in this regime the reaction takes place in a thin surface layer, with negligible effect of the external resistance if  $1 \ll \phi \ll \nu$ , or with the observed reaction rate  $\psi = (j+1)\nu$  controlled by external mass transfer resistance if  $\phi \gg \nu$ .

The previous analysis can also be used to deal with the problem of pore-mouth poisoning such that the catalytic activity, and therefore the reaction rate, is zero outside a radius  $x_p$ . The definitions of eqn (5), if  $u_p = u(x_p)$ , yield the relations,

$$\omega = (x_p/u_p)u_s(x_p), \quad \theta = \phi^2 x_p^2 u_p^{n-1}. \quad (17)$$

On the other hand, from the analysis of the region  $x_p < x < 1$  we obtain

$$\psi/(j+1) = \nu(1 - u_s) = u_p x_p^{j-1} \omega \quad (18)$$

and

$$u_p = u_s - \frac{\nu(1 - u_s)}{j-1} (x_p^{1-j} - 1). \quad (19)$$

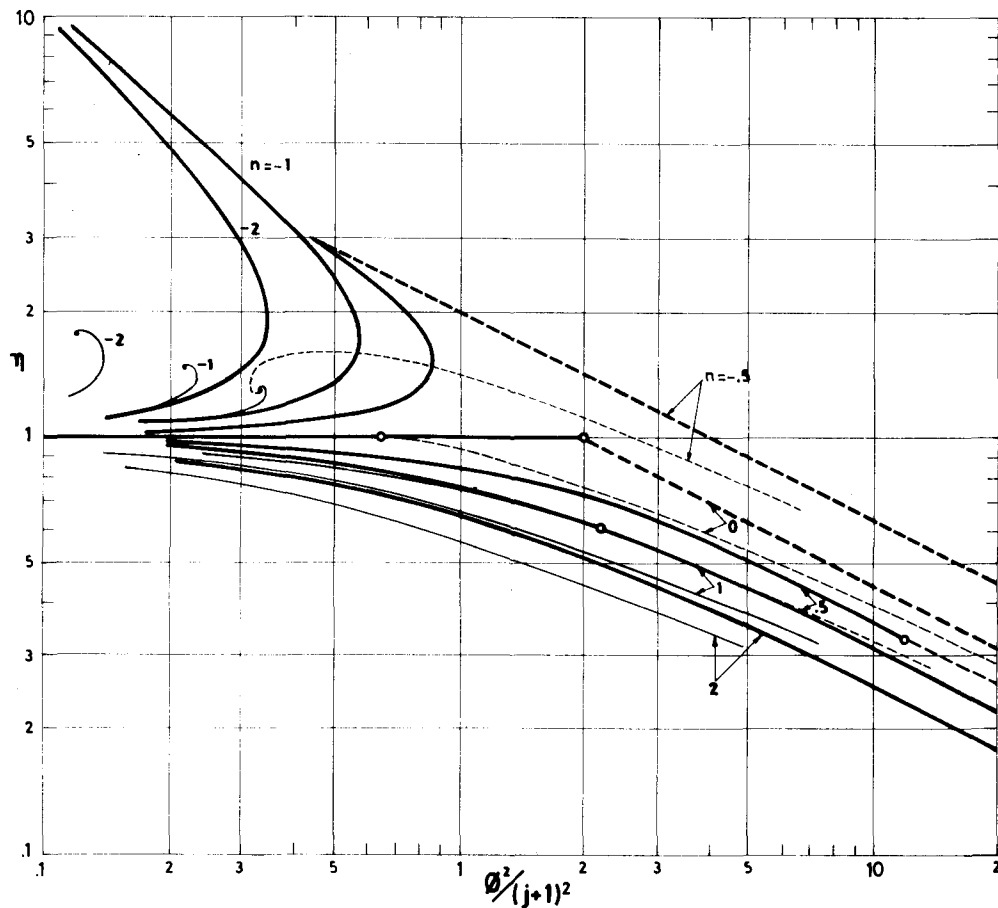


Fig. 2. The effectiveness factor in terms of  $\phi^2$  for spherical pellets with thin lines, and slabs with thick lines.

These relations enable us to calculate explicitly  $\omega$  in terms of  $\psi$ ,  $\nu$ ,  $x_p$  and  $j$ , and when used with the relation  $\theta(\omega, n, j)$  and the definition of  $\theta$  in eqn (17) allow us to calculate  $\phi = \phi(\psi, \gamma, j, n, x_p)$ . Thus if  $\phi_1(\psi, \nu, j, n)$  is the value of  $\omega$  for  $x_p = 1$ , then  $x_p \phi = \phi_1(\psi x_p^{1-j}, \nu, j, n)$  with  $\nu_e^{-1} = x_p^{j-1}/\nu + (1 - x_p^{j-1})/(j-1)$ . A more detailed description of this analysis and applications to non-isothermal and Langmuir-Hinshelwood reactions are given by Vega[5].

#### NOTATION

- $j$  = 0, 1 and 2 for slabs, cylinders and spheres, respectively  
 $n$  reaction order  
 $t = \ln(x/x_0)$   
 $u$  dimensionless concentration based on the interstitial value  
 $x$  dimensionless distance to the center of the particle  
 $x_0$  size of the region where  $u = 0$   
 $z = \ln(u/u_0)$

#### Greek symbols

- $\eta$  effectiveness factor,  $\eta = \psi/\phi^2$   
 $\theta$  variable defined in eqn (5)

$\nu$  Sherwood number

$\phi$  Thiele modulus

$\psi$  non-dimensional observable reaction rate, see eqn (3)

$\omega$  variable defined in eqn (5)

#### Subscripts

- 0 indicates concentration at the center of the particle  
 $c$  critical point of eqn (7), given by eqns (12)  
 $p$  position of the boundary of pre-mouth poisoning  
 $s$  refers to conditions at the particle surface

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